XIV. *Remarks on Mr.* Cavendiſh's *Experiments on Air. In a Letter from* Richard Kirwan, *Eſq. F. R. S. to Sir* Joſeph Banks, *Bart. P. R. S.*

Read Feb. 5, 1784.

SIR,

HAVING liſtened with much attention, and derived much uſeful information from the very curious experiments of Mr. CAVENDISH, read at our laſt meeting, it is with peculiar regret I feel myſelf withheld from yielding an intire aſſent to all he has advanced in his very ingenious paper; and it is with ſtill greater that I find myſelf obliged, by reaſon of the oppoſition of ſome of his deductions to thoſe I had the honour to lay before the ſociety about two years ago, to expoſe the reaſons of my diſſent, through your mediation, before this meeting.

In the paper already mentioned, read in April, 1782, I attributed the diminution of reſpirable air, obſerved in common phlogiſtic proceſſes, to the generation and abſorption of fixed air, which is now known to be an acid, and capable of being abſorbed by ſeveral ſubſtances. That fixed air was ſome how or other produced in phlogiſtic proceſſes, either by *ſeparation* or *compoſition*, I took for granted from the numerous experiments of Dr. PRIESTLEY; and among theſe I ſelected, as leaſt liable to objection, the Calcination of Metals, the decompoſi-

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tion of nitrous by mixture with reſpirable air, the phlogiſtication of reſpirable air by the electric ſpark, and, laſtly, that effected by amalgamation. In each of theſe inſtances Mr. CAVENDISH is of opinion, that the diminution of reſpirable air is owing to the production of water, which, according to him, is formed by the union of the phlogiſton, diſengaged in thoſe proceſſes, with the dephlogiſticated part of common air; and that fixed air is never produced in phlogiſtic proceſſes, except ſome animal or vegetable ſubſtance is concerned in the operation, from whoſe decompoſition it may ariſe. To which of theſe cauſes the diminution of reſpirable air is to be attributed, I ſhall now endeavour to elucidate.

Of the Calcination of Metals.

I attributed the diminution of air by the calcination of metals, to the converſion of the dephlogiſticated part of common air into fixed air, by reaſon of its union with the phlogiſton of the metal, for this plain reaſon, becauſe I find it acknowledged on all hands, that the calces of all the baſe metals yield fixed air, when ſufficiently heated. Mr. Cavendiſh allows the fact in general, but aſcribes the fixed air found in them to their long expoſure to the atmoſphere, in which he ſays fixed air pre-exiſts; but that it exiſts in common air in any quantity worth attending to, or is extracted from it in any degree, I take the liberty of denying, grounded on the following facts. Firſt, I have frequently agitated 18 cubic inches of common air in 2 of lime-water, and 2 of common air in 18 of lime-water, but could never perceive the ſlighteſt milkineſs; and yet the thouſandth part of a cubic inch of fixed air would thus be made ſenſible; for if a cubic inch of it be diſſolved in 3 ounces of water, a few drops of that water let into lime-water will produce a cloud. Mr. FONTANA ſays, he frequently agitated 1 cubic inch of Tincture of Turnſole in 7 or 800 of common air, without reddening it (23 ROZ. p. 188.); and yet, according to Mr. BERGMAN, 1 cubic inch of fixed air is ſufficient to redden 50 of Tincture of Turnſole (1 BERGM. 11.); from whence I am apt to think, that 700 cubic inches of common air do not even contain $\frac{1}{50}$th of a cubic inch of fixed air. Dr. WHYTT found that 12 ounces of ſtrong lime-water, being expoſed to the open air for 19 days, ſtill retained about 1 grain of lime, (on Lime-water, p. 32.). Now 12 ounces of ſtrong lime-water contain at moſt 9,5 grains of lime, and 1 grain of lime requires only 0,56 of a cubic inch of fixed air to precipitate it, the thermometer at 55 and the barometer at 29,5, as I have found. Therefore in 19 days this lime-water did not come in contact with more than four cubic inches of fixed air; yet it is certain that a large quantity of fixed air is continually diſengaged, and thrown into the atmoſphere, by various proceſſes, as putrefaction, combuſtion, &c. but it ſeems equally certain that it is either decompoſed, or more probably abſorbed by various bodies. Mr. FONTANA let looſe 20000 cubic inches of fixed air, in a room whoſe windows and doors were cloſed, yet in half an hour after he could not diſcover the leaſt trace of it (ibid.). Though fixed air perpetually oozes from the floor of the *Grotto del Cane*, yet at the diſtance of four or five feet from the ground none is found; animals may live, lights burn, &c. (Roz. Ibid. Mem. Stockh. 1775.). If diſtilled water be expoſed to the atmoſphere, it is never found to abſorb fixed air, but rather dephlogiſticated air, according to Mr. SCHEELE's experiments, which could never happen if the atmoſphere contained any ſenſible proportion of fixed air; nor has rain-water been ever found to contain any, which it certainly ſhould on the ſame hypotheſis; even Mr. CAVENDISH himſelf could find no fixed air in the reſiduum or products of about 1040 ounce meaſures of common air, which he burnt with inflammable air.

It is true, Dr. PRIESTLEY ſuppoſed common air to contain $\frac{1}{55}$ of its bulk of fixed air; but he drew this concluſion not from any direct experiment, but from the quantity of fixed air produced by breathing, which he at that time believed to have been barely precipitated, and not generated, an opinion which he has found reaſon to alter from his own experiments. I think I may therefore conclude, that the quantity of fixed air contained in the atmoſphere is abſolutely inappreciable.

Secondly, ſuppoſing the atmoſphere to contain a very ſmall proportion of fixed air, yet I do not think it can be inferred that metals, during their calcination, extract any, becauſe I find that lime expoſed to red heat ever ſo long extracts none, though it is formed by a calcination in open air, which laſts at leaſt as long as that of any metal; neither does precipitate *per ſe* attract any, though its calcination laſts ſeveral months; nor does this proceed from the want of affinity, for if a ſaturate ſolution of mercury in any of the acids be precipitated by a mild vegetable alkali, very little efferveſcence is perceived, and the precipitate weighs much more than the quantity of mercury employed, and that this increaſe of weight ariſes in part from the fixed air abſorbed will preſently be ſeen.

Since then metals may be calcined in cloſe veſſels, ſince they then abſorb one fourth part of the common air to which they are expoſed, ſince all metallic calces (except thoſe of mercury, which I ſhall preſently mention) yield fixed air, ſince common

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air contains ſcarce any fixed air; is it not apparent that the fixed air thus found was generated by the very act of calcination, by the union of the phlogiſton of the metal with the dephlogiſticated part of the common air, ſince after the operation the metal is deprived of its phlogiſton, and the air of its dephlogiſticated part?

But Mr. CAVENDISH objects, that no one has extracted fixed air from metals calcined in cloſe veſſels. To which I anſwer, that this further proof is difficult, and no way neceſſary; it is difficult, becauſe the operation can eaſily be performed only on ſmall quantities; it is unneceſſary, becauſe it differs from the operation in open air only by the quantities of the materials employed, in every other reſpect it is exactly the ſame. Since Mr. CAVENDISH ſuſpects the reſults are different, it is incumbent on him to ſhew that difference; but until then, according to Sir ISAAC NEWTON's ſecond rule, *to natural effects of the ſame kind the ſame cauſes are to be aſſigned, as far as it may be done*, that is, until experience points out ſome other cauſe.

It may further be urged, that precipitate *per ſe* yields only dephlogiſticated air, that minium alſo yields a large proportion of it. This difficulty I have formerly anſwered by aſſerting, that theſe calces are in fact united only to fixed air, and that they yield dephlogiſticated air, merely becauſe the fixed air is decompoſed by the total or partial revivification of the metallic ſubſtances; this I think may be demonſtrated by the following experiments. Let ſublimate corroſive ſingly be treated in any manner, it will not yield dephlogiſticated air (4 Pr. 240.); but let a ſolution of ſublimate corroſive be precipitated by a mild fixed alkali, this precipitate waſhed, dried, and diſtilled in a pneumatic apparatus, will yield dephlogiſticated air, and the mer-

mercury will be revived; but, if the ſolution of ſublimate corroſive be precipitated by lime-water, it ſeems no air will be produced. Here then we ſee, 1ſt, that the calx of mercury unites with fixed air; and, 2dly, that this fixed air is, during the revivification of the mercury, converted into dephlogiſticated air. Again: let one ounce of red precipitate, which, according to Mr. CAVENDISH, contains no nitrous acid, be diſtilled with two ounces of filings of iron; this quantity of precipitate, which, if diſtilled by itſelf, would yield 60 ounce meaſures of dephlogiſticated air, will, when diſtilled with this proportion of filings of iron, yield 40 ounce meaſures of fixed air, as Dr. PRIESTLEY has ſhewn in his laſt paper: whichever way this is explained, ſome or other of my opinions are confirmed; for either the mercurial calx is already combined with fixed air (which I believe to be the caſe), and this air paſſes undecompoſed, becauſe the mercury extracts phlogiſton from the iron; or it contains dephlogiſticated air, which is converted into fixed air by its union with the phlogiſton of the iron.

If precipitate *per ſe* be digeſted in marine acid, the mercury will be revived (3 BERGM. 415.). Now this calx does not dephlogiſticate the marine acid; for this acid, when dephlogiſticated, diſſolves mercury; how then does it revive it, if not by expelling the fixed air contained in it, which in the moment of its expulſion is decompoſed, leaving its phlogiſton to the mercury, which is thereby revived?

Again: if litharge be heated in a gun-barrel, it will afford more fixed and leſs dephlogiſticated air than if heated in glaſs or earthen veſſels. Does not this happen, becauſe the calx of lead, receiving ſome phlogiſton from the metal, does not dephlogiſticate ſo great a proportion of the fixed air as it otherwiſe would?

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Further: there is no ſubſtance which yields dephlogiſticated air, but yields alſo fixed air, even precipitate *per ſe* not excepted; (3 PRIEST. 16.) and what is remarkable, they all yield fixed air firſt, and dephlogiſticated air only towards the end of the proceſs. Does not this happen becauſe metallic calces attract phlogiſton ſo much more ſtrongly, as they are more heated? Thus many calciform iron ores become magnetic by calcination, though they were not ſo before; ſo alſo do all the calces of iron when expoſed to the focus of a burning glaſs (5 Dict. Chy. 179). Thus mercury cannot be calcined but in a heat inferior to that in which it boils; thus minium cannot be formed but in a moderate heat, and if heated ſtill more it returns to the ſtate of maſſicot, in which it was before it became minium, and much of it is reduced. So if a ſolution of luna cornea in volatile alkali be triturated with mercury, the ſilver will be revived, and the marine acid unite to the mercury, which ſhews this acid has a ſtronger attraction to Mercury than to ſilver; yet if ſublimate corroſive and ſilver be diſtilled in a ſtrong heat, the mercury will be revived, and the marine acid unite to the ſilver, which ſhews that the attraction of mercury to phlogiſton increaſes with the heat applied.

Before I conclude this head, I will mention another experiment, which I think deciſive in favour of my opinion of the compoſition of fixed air. If filings of zinc be digeſted in a cauſtic fixed alkali in a gentle heat, the zinc will be diſſolved with efferveſcence, and the alkali will be rendered in great meaſure mild. But if, inſtead of filings of zinc, flowers of zinc be uſed, and treated in the ſame manner, there will be no ſolution, and the alkali will remain cauſtic. In the firſt caſe the efferveſcence ariſes from the production of inflammable air, which

which phlogiſticates the common air contiguous to it, and produces fixed air, which is immediately abſorbed by the alkali, and renders it mild. In the ſecond caſe, no inflammable air is produced, the common air is not phlogiſticated, and conſequently the alkali remains cauſtic*. This experiment alſo proves that metallic calces attract fixed air more ſtrongly than alkalies attract it; for the calces of zinc are known to contain fixed air, and yet alkalies digeſted with them remain cauſtic; and this accounts for the ſlight turbidity of lime-water when metals are calcined over it; for as ſoon as the phlogiſton is diſengaged from the metal, and before it has abſorbed the whole quantity of fire requiſite to throw it into the form of inflammable air, it meets with the dephlogiſticated part of the common air on the ſurface of the metal, and there forms fixed air, which is inſtantly abſorbed by the calx with which it is in contact, ſo that it is not to be wondered that it does not unite to the lime from which it is diſtant.

Of the Decompoſition of Nitrous Air by mixture with Common Air.

AS ſoon as I had heard Mr. CAVENDISH's paper read, I ſet about trying whether lime would be precipitated from lime-water during the proceſs, an experiment I had never made before with common air, taking it for granted that it was ſo, from the repeated experiments of Dr. PRIESTLEY, and indeed of all others who had treated this ſubject †: and, in effect,

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[*] See Mr. LASSONE's Experiments on zinc. Mem. Par. 1777. p. 7 & 8.

[†] See 1 Pr. 114. 189. 2 Pr. 218. Font. Recherches Phyſ. p. 77. 1 Chy. Dij. 324.

when I made the experiment with nitrous air prepared and confined by the water of my tub, I found lime-water admitted to it inſtantly precipitated. But after I had read Mr. CAVENDISH's paper, which he had the politeneſs to permit me, and had, according to his direction, received the nitrous air over lime-water, I did not then perceive the leaſt milkineſs after admitting common air. After 12 hours I indeed perceived a whitiſh duſt, on the bottom of the glaſs veſſel in which I made the experiment, which I cannot aſſure to be calcareous; and, on breathing into the lime-water, an evident milkineſs enſued; ſo that I little doubt but the precipitation I obſerved in the firſt experiment aroſe from the decompoſition of the aerial ſelenite contained in the water of the tub. And it is very poſſible that the precipitation of lime, which I perceived ſome years ago on mixing dephlogiſticated air and nitrous air, might have ariſen from the ſame cauſe, or from fixed air pre-contained in the dephlogiſticated, as this laſt had not been waſhed in lime-water. Yet I do not think the failure of this experiment at all concluſive againſt the ſuppoſed production of fixed air on this occaſion, becauſe the quantity of fixed air is ſo ſmall, that it may well be ſuppoſed to unite to the nitrous ſelenite formed in the lime-water. It is well known that a ſmall quantity of fixed air is capable of uniting to all neutral ſalts: thus Dr. PRIESTLEY has extracted it from tartar vitriolate and alum, (2 PR. 115, 116.) and gypſum, (2 PR. 80.); and Dr. MAC BRIDE found it in nitre and common ſalt, though in ſmall quantity. But to try whether nitrous ſelenite would attract any, I made a ſolution of chalk in nitrous acid, which, when ſaturate, weighed 381,25 grains; but, being expoſed to the air for a few hours, it weighed 382,25. I afterwards took a very dilute nitrous acid, in which an acid taſte was barely perceptible, and impregnated it with a very ſmall proportion

portion of fixed air, and then let fall a few drops of it into lime-water; not the ſmalleſt cloud was perceived, and yet when I breathed into it afterwards it became milky in a few ſeconds; ſo that this experiment is perfectly analogous to that in which nitrous and common air were mixed.

But if nitrous air and common air be mixed over dry mercury, the reſult is intirely adverſe to the opinion of Mr. CAVENDISH, and favourable to mine; for in this caſe the common air is not at all diminiſhed until water is admitted to it, and the mixture agitated a few minutes, and then the diminution is nearly the ſame as if the mixture were made over water. Thus when I mixed two cubic inches of common air with one of nitrous air, they occupied the ſpace of two inches and one-eighth, and the ſurface of the mercury was immediately calcined; which ſhews that the inch of nitrous air was decompoſed, and produced nitrous acid; but the common air was undiminiſhed; and the one eighth of an inch over and above the two inches of common air, proceeded from an addition of new nitrous air, formed by the corroſion of the ſurface of the mercury. That the common air ſhould remain undiminiſhed is eaſily explained in my ſyſtem, becauſe fixed air is formed, which, on this occaſion, muſt remain unabſorbed, at leaſt for a long time, as there is nothing at hand that can immediately receive it; and hence, if water be admitted ſoon after the mixture of both airs, the diminution will be nearly the ſame as if the mixture had been originally made over water, though not exactly the ſame; becauſe the nitrous air, produced by the union of the newly formed nitrous acid with the mercury, is not entirely abſorbable by water. But, in Mr. CAVENDISH's hypotheſis, the common air ſhould be diminiſhed juſt as much as if the mixture were made over water; for, according to him,

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this diminution ariſes from the converſion of the dephlogiſticated part of the common air into water, which water ſhould immediately unite to the nitrous ſalt of mercury, and leave the common air leſſened in its bulk by a portion commenſurate to that converted into water, or, if he will not allow the water to have immediately united to the mercurial ſalt, at leaſt by the difference of the bulk of the water produced, and that of an equal weight of the common air converted into it: but neither happens; for the common air is not at all diminiſhed; nor can he explain, conſiſtently with his ſyſtem, why the admiſſion of water ſhould immediately produce a diminution in the common air, as, according to him, it contains nothing that can be abſorbed. Dr. PRIESTLEY has remarked, that if a mixture of both airs be ſuffered to ſtand ſeveral hours, even the admiſſion of water will produce no diminution. This is owing to two cauſes; 1ſt, becauſe a large quantity of nitrous air is produced, by the continued action of the concentrated nitrous acid newly formed; and, 2dly, becauſe the fixed air, on whoſe abſorption the diminution depends, is abſorbed by the mercurial ſalt, as may be inferred from the experiment in 1 LAVOISIER, p. 248.

Of the Diminution of Common Air by the Electric Spark.

Of all the inſtances of the artificial production of fixed air, by the union of phlogiſton with the dephlogiſticated part of common air, there is none perhaps ſo convincing, as that exhibited by taking the electric ſpark through common air, over a ſolution of litmus, or lime-water; for the common air is diminiſhed one fourth, the litmus reddened, and the lime-water precipitated. Mr. CAVENDISH indeed attributes the redneſs of the litmus to fixed air; but he thinks it proceeds from a decompoſition of ſome part of the vegetable juice, as all vegetable juices contain fixed air. Yet that ſuch a decompoſition does not take place, I think may be inferred from the following reaſons: firſt, if the electric ſpark be taken through phlogiſticated or inflammable air confined by litmus, no redneſs is produced, the air not being in the leaſt diminiſhed; and, 2dly, if the litmus were decompoſed, inflammable air ſhould be produced as well as fixed air; and then there ſhould be an addition of bulk inſtead of a diminution; but what ſets the origin of the fixed air from the phlogiſtication of the common air beyond all doubt is, that if lime-water be uſed inſtead of litmus, the diminution is the ſame, and the lime is precipitated. Here Mr. CAVENDISH ſays, the fixed air proceeds either from *ſome dirt in the tube*; a ſuppoſition, which, being neither neceſſary nor probable, is not admiſſible; or elſe *from ſome combuſtible matter in the lime*; but lime contains no combuſtible matter, except perhaps phlogiſton, which cannot produce fixed air but by uniting to the common air, according to my ſuppoſition; but it is much more probable, that the diminution does not ariſe from any phlogiſton in the lime, as it is exactly the ſame whether lime-water be uſed or not; and the lime does not appear to be in the leaſt altered, and in fact contains ſcarce any phlogiſton.

Of the diminution of Common Air, by the Amalgamation of Mercury and Lead.

I attributed this diminution to the phlogiſtication of the common air by the proceſs of amalgamation, and the conſequent production and abſorption of fixed air. On this Mr. CAVENDISH

VENDISH obſerves, "that mercury, fouled by the addition of "lead or tin, depoſits a powder which conſiſts in great meaſure "of the calx of the metal: he found alſo, that ſome powder of "this ſort contained fixed air; but it is not clear that this air "was produced by the phlogiſtication of the air in which the "mercury was ſhaken, as the powder was not prepared on "purpoſe, but was formed from mercury fouled by having "been uſed for various purpoſes, and may therefore contain "other impurities, beſides the metallic calx." On this I remark, that Dr. PRIESTLEY did not indeed at firſt prepare this powder on purpoſe; but he afterwards did ſo prepare it (4 PRIEST. p. 148, 149.) and obtained a powder exactly of the ſame ſort; and it is certain that the fixed air found in it proceeded from the common air, both becauſe metallic calces, not formed by amalgamation, will not unite with mercury, as is well known; and becauſe this calx cannot be formed by agitation of the mercury and lead, in phlogiſticated, inflammable, or any other air which is not reſpirable; and the fixed air cannot proceed from any impurity, as mercury will not unite in its running form to any other but metallic ſubſtances, which it always partially dephlogiſticates, like other menſtruums (3 Chy. Dijon, 425.).

Of the Diminution of Reſpirable Air by Combuſtion.

Though I have no doubt but the diminution of reſpirable air, by the combuſtion of ſulphur and phoſphorus, proceeds alſo in great meaſure from the production and abſorption of fixed air, yet I avoided mentioning this operation, as the preſence of a ſtronger acid renders the preſence of a weaker impoſſible to be proved, more eſpecially, as both theſe acids precipitate lime from lime-water; but the great increaſe of weight which the phoſphoric acid gains is a ſtrong additional inducement to think that it abſorbs fixed air. During the combuſtion of vegetable ſubſtances, I think it highly probable that fixed air is formed, both from my own experiments on the combuſtion of wax candles, and that mentioned in the firſt volume of Dr. PRIESTLEY's Obſervations, p. 136; but when inflammable air from metals and dephlogiſticated air are fired, as a great diminution takes place, and yet no fixed air is found, I am nearly convinced, by Mr. CAVENDISH's experiments, that water is really produced; nor am I ſurprized that, in this inſtance, the union of phlogiſton and dephlogiſticated air ſhould form a compound very different from that which it forms in other inſtances of phlogiſtication, but ſhould rather be led to expect it *a priori*; for in this caſe the phlogiſton is in its moſt rarefied known ſtate, and unites to dephlogiſticated air, the ſubſtance to which it has the greateſt affinity, in circumſtances the moſt favourable to the cloſeſt and moſt intimate union; for both, in the act of inflammation, are rarefied to the higheſt degree; both give out their ſpecific fire, the great obſtacle to their union, it being by the inflammation converted into *ſenſible* heat (a circumſtance which, in my opinion, conſtitutes the very eſſence of flame); the reſulting compound having then loſt the greateſt part of its ſpecific fire, is neceſſarily reduced, according to Dr. BLACK's theory, into a denſer ſtate, which the preſent experiment ſhews to be water; whereas, in common caſes of combuſtion, the phlogiſton being denſer and leſs divided, unites leſs intimately with the dephlogiſticated part of common air, conſequently expels leſs of its ſpecific fire, and therefore forms leſs denſe compounds, *viz.* fixed and phlogiſticated airs; and ſo much the more, as a great part intirely eſcapes combuſtion; but it ſeems probable

probable that in very ſtrong and bright inflammations, the union is more perfect, and water formed.

Water being then the reſult of the cloſeſt and moſt intimate union of dephlogiſticated air and phlogiſton, it ſeems to me very improbable, that it is ever decompoſed by the affinity of any acid to phlogiſton, as all the experiments hitherto made ſeem to prove, that phlogiſton has a ſtronger affinity to dephlogiſticated air than to any other ſubſtance, except hot metallic calces; and theſe, in my opinion, are incapable of forming any union with water, except as far as they are ſaline, but they never can be reduced by it. So alſo water is incapable of uniting with any more phlogiſton, as ſulphur is, both being already ſaturated.

Mr. CAVENDISH is inclined to think, that pure inflammable air is not pure phlogiſton, becauſe it does not immediately unite with dephlogiſticated air, when both airs are ſimply mixed with each other; this reaſon ſeems to me of no moment, becauſe I ſee ſeveral other ſubſtances, that have the ſtrongeſt affinity to each other, refuſe to unite ſuddenly, or even at all, through the very ſame cauſe that dephlogiſticated and inflammable airs refuſe to unite; *viz.* on account of the ſpecific fire which they contain, and muſt loſe, before ſuch union can take place: thus fixed air will never unite to dry lime, though they be kept ever ſo long together; thus, if water be poured on the ſtrongeſt oil of vitriol, they will remain ſeveral weeks in contact, without uniting, as I myſelf have experienced; and yet, in both caſes, the ſpecific fire need be expelled only from one of the ſubſtances, and not from both: but after a long time they will unite; ſo alſo will inflammable and dephlogiſticated air, as Dr. PRIESTLEY has diſcovered ſince his laſt publication.

That phlogiſticated air ſhould conſiſt of ſuperſaturated nitrous air, I think improbable, as it retains its phlogiſton much more ſtrongly than nitrous air, which, according to the general laws of affinities, it ſhould not, if it contained an exceſs of phlogiſton; and as Dr. Priestley and Mr. Fontana repeatedly aſſure us, they have converted it into common air, by waſhing it in water, in contact with the atmoſphere. I am, *&c.*

London,
Jan. 29, 1784.

R. Kirwan.